MONITORING THE EXPOSURE OF WORKERS DURING THE THE MIXING, LOADING AND APPLICATION OF AZINPHOSMETHYL TO STONE FRUIT

By

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<u>ABSTRACT</u>

The potential inhalation and dermal exposure of two workers during mixing, loading and application of azinphosmethyl to stone fruit were measured in Fresno County in May of 1988. Two types of applicator exposures were monitored: (1) ground application with a low volume, electrostatic sprayer and (2) ground application with a conventional air blast sprayer. The worker operating the low volume sprayer (worker 1) was monitored for 7.5 hours and the worker operating the air blast sprayer (worker 2) was monitored for 3.5 hours. Both workers performed mixing, loading and application tasks. Potential inhalation exposures were monitored by sampling the air in the workers' breathing zone, outside their respirators. The estimated potential inhalation exposures were 294 ug/m^3 (low volume sprayer) and 427.5 ug/m^3 (air blast sprayer). Dermal exposures (8), were measured by analyses of a long-sleeved, 100% cotton, knit shirt worn next to the skin under the Tyvek^R coverall, knee-length cotton/acrylic blend socks worn in place of the workers' normal socks, two gauze sampling patches attached to the thigh area of the workers' pants, (under the Tyvek R coverall), a cellulose fiber bouffant cap, a handwash and composite face and neck wipes. The dermal exposures for the work period were 1000.0 ug and 1300.0 ug for worker 1 and 2, respectively. Blood samples were drawn from worker I before and after the exposure period and analyzed for cholinesterase levels. The red blood cell and plasma cholinesterase levels showed no significant decrease after exposure. Results showed that the

worker operating the air blast sprayer had both a greater exposure per hour and per pound material applied than did the worker operating the low volume sprayer (371.0 ug/hr and 310.0 ug/lb for worker 2 compared to 133.0 ug/hr and 51.0 ug/lb for worker 1). Future studies are required to confirm the estimates of exposure measured during this study.

INTRODUCTION

Azinphosmethyl is a highly toxic organophosphate pesticide and cholinesterase inhibitor. It has an acute oral LD $_{50}$ of 11 mg/kg and a dermal LD $_{50}$ of 220 mg/kg (2). The compound is widely used to control certain insects on stone fruits. Organophosphate pesticides and their corresponding oxidation products are known to cause worker illness through reduction of cholinesterase enzyme activity when toxic exposure occurs. In assessing the hazard to workers who are mixing, loading and applying azinphosmethyl, an accurate estimate of exposure is necessary. This study employs both dermal and inhalation monitoring of two workers who operate different types of application equipment.

MATERIALS AND METHODS

With the cooperation of the Fresno Agricultural Commissioner and a local grower, we monitored the application of azinphosmethyl to three stone fruit The product used was Guthion^R (EPA reg. number 3125-379), a orchards. wettable powder formulation with 35% active ingredient. It is packaged in boxes containing five 1.38 pound soluble packets. Two types of spray equipment were used to apply the product. A low volume electrostatic sprayer was used to treat two orchards: (1) 9.50 acres of nectarines at 0.7 1bs. a.i. in 20 gallons of water per acre, and (2) 9.14 acres of peaches at 1.4 lbs. a.i. in 20 gallons of water per acre. A conventional air blast sprayer applied azinphosmethyl to an 8-acre nectarine orchard at the rate of 0.53 lbs. active ingredient (a.i.) per acre in 100 gallons of water. No other materials were applied with the azinphosmethyl. A tank mix sample was drawn from the first mix load of each of the three applications, stored in a NalgeneR bottle and placed immediately on dry ice. The two workers who applied the azinphosmethyl also performed the mixing and loading tasks.

The method for dermal monitoring was modified from Durham and Wolfe (1) and Maddy, et al. (3). Prior to beginning the mixing and loading, each worker was provided with clothing and equipment for the dermal and inhalation These consisted of: a long-sleeved, 100% cotton, knit shirt worn next to the skin, a pair of knee-length athletic type socks, two gauze sampling patches, each in foil-backed cardboard holder (exposed area = 23.75 cm² each) mounted on the outside of the pants on the thigh area, a cellulose fiber bouffant cap, and a personal air sampling pump with a flow rate of 2 liters/min. drawing air through an SKC West type A glass fiber filter (37 mm diameter, 0.8 micron pore size). The filter cassette was positioned in the workers' breathing zone. Both workers wore TyvekR coveralls over their clothing and wore rubber boots, rubber gloves and a half-face respirator throughout the monitoring period. The exposure period began with the mixing and loading of the first load of material into each sprayer. This took approximately 45 minutes. One worker operated the low volume sprayer: he worked for 7.5 hours spraying two loads (6.65 pounds

a.i.) at 0.7 lb/acre and two loads (12.8 pounds a.i.) at 1.4 lb/acre, for a total of 19.5 pounds. The second worker operated the air blast sprayer: he worked for 3.5 hours spraying four loads (4.2 pounds a.i.) at 0.53 lb/acre. The applications were conducted simultaneously in adjacent plots, to trees similar in height, spacing and canopy. The exposure monitoring ended at the completion of each worker's applications.

At the end of the work period, a handwash and a composite face and neck wipe sample were collected from both workers. They washed their hands in 500 mls of a 1% dioctyl sodium sulfosuccinate solution for one minute. The solution was then poured into a Nalgene^R bottle and stored on dry ice. The workers used two moist towelettes (Chubs^R brand) to wipe their face and neck regions. The towelettes were placed in a glass jar, capped with foil, sealed and placed on dry ice. The filter cassettes and dermal monitoring clothing (socks, shirts, gauze patches and bouffant caps) were then collected. The shirts were cut at the armhole to create separate arm and torso samples. All clothing samples were placed in Ziploc^R bags, sealed and stored on dry ice. All samples were shipped to the California Department of Food and Agriculture Chemistry Laboratory Services, Worker Health and Safety Section, in Sacramento, for analysis.

Samples were extracted using ethyl acetate, dried with anhydrous sodium sulfate and diluted as necessary. Laboratory spike recoveries were 94 - 110%. Two microliters of sample were injected and analyzed on a 10.0 m x 0.53 mm i.d. column coated with 50% phenyl methyl silicone, using a Hewlett-Packard 5880A gas chromatograph with electron capture detector. Column temperature was 250°C. The injection port temperature was 225°C and detector temperature was 300°C. Helium carrier gas flow rate was set at 15 ml/min and NPD helium make-up gas set at 5 ml/min. Using these conditions, azinphosmethyl has a retention time of 4.2 minutes.

The minimum detection levels (MDL) for the different matrices and the field spike recoveries are reported in Appendix I. Results were not adjusted to these recoveries. Where results were reported as none detected, one-half the MDL was used. The sock, shirt, cap, gauze patch, face and neck wipes and handwash results were added to give the daily dermal exposure for the respective body regions. The exposure to the hips and thighs was extrapolated from patch data to body region, assuming 10% clothing penetration (1,8).

Worker 1 was monitored for red blood cell and plasma cholinesterase levels. The blood draws and analyses of red blood cell and plasma cholinesterase levels were performed by an independent certified laboratory.

RESULTS

The results of the tank mix analyses confirmed the application rates within 20%. The results of the dermal and inhalation monitoring are reported in Table I. The primary exposure was dermal, with the potential inhalation exposure, if no respirator were worn, contributing about 25% to the total potential exposure for each worker. The inhalation exposure reflects a calculation based on measurement of the azinphosmethyl concentration outside the respirator, minutes worked, and a breathing rate of 25 L/min (4). Assuming a 90% protection factor for the respirator (6), the contribution

from inhalation exposure is low (about 3% of total exposure). Worker 1, operating the low volume sprayer, worked twice as long as worker 2, operating the dilute sprayer and applied nearly 5 times the amount of material as did worker 2 and received 77% the dermal exposure (1000.0 ug compared to 1300.0 ug). Worker 1 had 15% of his exposure to the regions covered by the shirt and socks. Worker 2, operating the air blast sprayer, received 79% of his exposure to the areas covered by the shirt and socks (1032 ug). Worker 1 received 66% of his exposure (661 ug) to the head area, as measured by azinphosmethyl residues on the cap. For worker 2, the cap contributed only 9% (116 ug) to his total exposure. Worker 1 received a greater contribution to total exposure from face and neck wipe residues (15.0%) than did worker 2 (5.5%). The contribution from handwashes to total exposure was similar for both workers at 3.5% for worker 1 and 6% for worker Both workers had less than 1% contribution to total exposure from residues measured on the thigh patches.

Results of the follow-up blood sampling for worker 1 showed his plasma cholinesterase level to be 101% of his baseline level and his RBC level to be 91% of his baseline. These levels are within normal limits for biological and analytical variation (7).

DISCUSSION AND CONCLUSIONS

In this study, there appeared to be distinct differences in both the amount and distribution of azinphosmethyl exposure by type of application Worker 1 worked twice as long as worker 2, applying nearly 5 times the amount of material that worker 2 applied and received overall 77% the dermal exposure of worker 2. On per hour basis, worker 1 received 133.0 ug and worker 2, about three times the exposure, at 371.0 ug. comparing ug total exposure to the amount of active ingredient sprayed. worker 1 received 51.0 ug exposure per pound azinphosmethyl, about 1/6 the amount of worker 2, who received 310.0 ug per pound azinphosmethyl applied. Worker 1 had the greatest percent of total exposure to the head region (66%), while worker 2 had the greatest percent exposure to the arms (54%). Observation of the workers during all phases of mixing, loading and application did not indicate any differences in task performance that would explain the variation in amount and distribution of exposure. If these data represent an accurate assessment of the pattern of exposure for these two application methods, it appears that a low volume application results in less exposure than an air blast application. It appears that wearing a hat or hood while operating a low volume sprayer could result in reducing exposures up to 75%, while wearing plastic sleeve protectors while operating an air blast sprayer could reduce exposure by 50%. This study monitored only one work period with each type of sprayer; future studies require the monitoring of a statistically significant number of applications with each type of sprayer to confirm the observations from this study. future studies should include blood and urinary metabolite monitoring for all workers involved to complete the exposure assessment.

Daily Dermal and Inhalation Exposure to Azinphosmethyl

| | ug/lb applied | 51.0 | 310.0 | |
|------------------------|----------------|-------|-------|------|
| | ug/hour | 133.0 | 371.0 | |
| | <u>Air</u> c | 294 | 427.5 | |
| Dermal <u>Total</u> | | 1000 | 1300 | 1 |
| ug/sample | Hand | 35 | 62 | |
| | Face/Neck | 151 | 72 | 1 |
| | Cap | 199 | 116 | |
| | <u>Thigh</u> b | 2.7 | 1.6 | |
| | Sock | p09 | 61 | |
| | Arm | 30q | 701 | |
| | Torso | p09 | 270 | |
| | Workera | | 2 | |

a Worker 1 operated the low volume sprayer, worked 7.5 hours, sprayed 19.5 lb a.i. Worker 2 operated the air blast sprayer, worked 3.5 hours, sprayed 4.2 lb a.i.

b Extrapolated from patch data to body region x 10% clothing penetration

c Calculated based on 25 L/min breathing rate and minutes worked

d Results reported as none detected; these values represent 1/2 the MDL

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APPENDIX I

Minimum Detection Levels, ug/sample

| Shirt, torso section | 120 |
|----------------------|------|
| Shirt, arm section | 60 |
| Socks | 60 |
| Gauze patch | 0.3 |
| Bouffant cap | 0.5 |
| Wipes | 0.2 |
| Handwash | 0.5 |
| Air Filter | 0.12 |

Field Spike Recoveries, in %

| 98-102 |
|-----------|
| no sample |
| 86-106 |
| 93-95 |
| no sample |
| 97 |
| no sample |
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